

LIGHT SCATTERING BY AN INTENSE LIGHT BEAM

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A classical theory of non-linear light scattering as can occur in an isotropic medium illuminated with a very intense light beam, *e. g.* from a laser, is developed and applied to scattering systems consisting of molecules (i) optically isotropic or (ii) tetrahedral or (iii) axially symmetric with a centre of inversion or (iv) axially symmetric without centre of inversion. Numerical evaluations are effected and yield a non-linear variation in the depolarization ratio D , accessible to detection in chloroform if illuminated with light of intensity not less than $I = 10^8$ e. s. u; in other substances (*e. g.* CS_2), variations of D will be observable on applying light of much greater intensity.

1. Introduction

The rapid development of lasers — sources of a strongly monochromatic and coherent light wave of great power flux — provide increasingly wide possibilities for the investigation of optical harmonics and various non-linear optical effects (see Braunstein 1962, Kleinman 1962, Armstrong *et. al.* 1962, Bloembergen and Pershan 1962, Loudon 1962, Kogan 1962, Franken and Ward 1963, McKenna and Platzman 1963, Karpman 1963).

One of the non-linear effects in which non-linear interaction between light and matter comes to the fore consists in the non-linear molecular scattering of light. Phenomenologically, the effect resides in the fact that the intensity of the light scattered by an isotropic medium can, in general, be a non-linear function of the intensity I , if sufficiently great, of the incident light. Thus, $I_n = AI + BI^2 + CI^3 + \dots$, where A determines linear Rayleigh scattering and B , C — nonlinear light scattering. From a molecular point of view, the physical meaning of A is well-known from the linear theories of light scattering (see Cabannes 1929, Bhagavantam 1942), whereas B derives in general from the effect of optical molecular hyperpolarizability (nonlinear polarization of the molecules in the strong electric field of the light wave) and from that of optical molecular orientation (orientation of the ellipsoid

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of molecular polarizability in the electric field of the light wave). Since the days of Lord Rayleigh, it has been known that the coefficient of linear scattering A contains the factor ω^4 with the fundamental frequency ω , whereas B contains moreover a term in $(2\omega)^4$ resulting from the second harmonic and C — a term in $(3\omega)^4$ resulting from the third. In inert gases or in ones consisting of isotropically polarizable molecules, non-linear light scattering is due to the effect of hyperpolarizability alone (Kielich 1961), while in gases consisting of anisotropic molecules it arises through both these effects, their mutual ratio depending numerically on the kind of symmetry of the molecules and on whether the latter are strongly or weakly hyperpolarizable. If the molecules are strongly anisotropic and possess a centre of inversion, the predominant role is played by the effect of molecular orientation (Kielich 1963 a, Piekara and Kielich 1963). Obviously, if the light oscillation frequency lies near absorption bands, the optical hyperpolarizability effect may be predominant in all cases (Kielich 1963 b). Either effect — that of optical hyperpolarizability and that of optical molecular orientation — gives rise to optical birefringence in isotropic bodies (Buckingham 1956) and electro-optical saturation in non-dipolar substances (Piekara and Kielich 1958, 1959).

Obviously the case is of greater interest when upon the scattered light produced by a light wave of frequency ω_1 and of low intensity there is incident another light wave of frequency ω_2 and of an intensity sufficiently great for the gas molecules to undergo non-linear polarization in its electric field (Kielich 1963 b). Apart from the frequency-dependence, the problem is to some extent analogous with the effect of an intense *DC* electric field on molecular light scattering (Rocard 1928, Andrews and Buckingham 1960, Kielich 1961, 1963 a).

The present paper is intended by the author as an extension of his earlier, linear theory of molecular light scattering (Kielich 1960) to the case of the non-linear scattering produced in an isotropic medium by a single light beam of very great intensity. We shall first derive a fundamental equation for the intensity of the non-linearly polarized light, whence general formulas will be obtained for the non-linear variation of the depolarization ratio D and of Rayleigh's ratio S . The discussion of the latter formulas is restricted to scattering systems of molecules that are spherically symmetrical, or tetrahedrally symmetrical, or axially symmetrical with or without a centre of inversion. To avoid complicating the final results, intermolecular angular correlations are neglected; albeit, in some cases, radial correlations are taken into account. Neither, for simplicity, is the effect of the molecular field on the induced electric moment considered. Such simplifications allowed to obtain the final results in a form well-adapted to direct numerical evaluations. The evaluations predict, in the case of molecules having a centre of inversion, very small changes in depolarization ratio and Rayleigh's ratio requiring for their detection an extremely intense light beam, whereas in the case of substances consisting of molecules without a centre of inversion, such as *e. g.* chloroform, non-linear variations of D or S accessible to observation already at an intensity of $I = 10^8$ esu of the light beam. From the results of the present theory, investigation of non-linearly scattered light is expected to provide direct information concerning the coefficients determining the non-linear polarization of the molecules under consideration.

2. Fundamental equation for the intensity of nonlinearly scattered light

We consider a classical system of N identical, optically anisotropic molecules in a volume V . Let the system be immersed in the oscillating electric field $\mathbf{E} = \mathring{\mathbf{E}} \cos \omega t$ of an incident plane light wave. We assume that the wavelength $\lambda = 2\pi c/\omega$ of this wave is large with respect to the distances between mutually interacting molecules and at the same time its oscillation frequency ω to be far remote from the electronic absorption band of the substance.

The oscillating electric field induces in the p -th molecule (and in all other molecules of volume V) a dipole moment $\mathbf{m}^{(p)}$. In the case of a weak electric field, $\mathbf{m}^{(p)}$ is linearly dependent on \mathbf{E} . At sufficiently high field strengths, however, the molecules experience in addition to linear polarization, a nonlinear polarization, and the α -component of $\mathbf{m}^{(p)}$ may be expressed in the form (see Appendix A)

$$m_{\alpha}^{(p)} = \alpha_{\alpha\beta}^{(p)} \mathring{E}_{\beta} \cos \omega t + \frac{1}{4} (\beta_{\alpha\beta\gamma}^{(p)} + \beta_{\alpha\beta\gamma}^{(p)} \cos 2\omega t) \mathring{E}_{\beta} \mathring{E}_{\gamma} + \\ + \frac{1}{24} (3\gamma_{\beta\beta\gamma\delta}^{(p)} \cos \omega t + \gamma_{\alpha\beta\gamma\delta}^{\prime(p)} \cos 3\omega t) \mathring{E}_{\beta} \mathring{E}_{\gamma} \mathring{E}_{\delta} + \dots, \quad (1)$$

where $\alpha_{\alpha\beta}^{(p)}$ is the optical polarizability tensor of the p -th isolated molecule and $\beta_{\alpha\beta\gamma}^{(p)}$ and $\gamma_{\alpha\beta\gamma\delta}^{(p)}, \dots$ are the tensors of its hyperpolarizability describing departures from the linear polarization law (see Born 1933 and Buckingham and Pople 1955). In the case of optically inactive substances and throughout spectral ranges widely remote from those in which absorption appears, the tensors $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are symmetric in all suffixes and real. The frequency-dependence of the above mentioned tensors is discussed in Appendix A.

Suppose \mathbf{n} is a unit vector describing the direction of the oscillations in the scattered light observed at considerable distances R_0 from the centre of volume V ; obviously, \mathbf{n} is perpendicular to the observation vector \mathbf{R}_0 . The n -component of the intensity of the light scattered is given, in the electric dipole approximation, by

$$I_n = \frac{1}{c^4 R_0^2} \langle \overline{\overline{\mathbf{M}_{\sigma} \mathbf{M}_{\tau} n_{\sigma} n_{\tau}}} \rangle_E, \quad (2)$$

wherein

$$\mathbf{M} = \sum_{p=1}^N \mathbf{m}^{(p)} \quad (3)$$

is the total dipole moment induced in the system of volume V by the electric field \mathbf{E} of the incident light wave.

The horizontal line ——— t in Eq. (2) denotes the time average and the brackets $\langle \rangle_E$ stand for the classical statistical average in the presence of the electric field E at equilibrium of the system at temperature T ,

$$\langle \Phi \rangle_E = \frac{\int \Phi(\tau, \mathbf{E}) \exp \left\{ -\frac{U(\tau, \mathbf{E})}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{U(\tau, \mathbf{E})}{kT} \right\} d\tau}, \quad (4)$$

with $U(\tau, \mathbf{E})$ denoting the total potential energy of the system when its molecules are at configuration τ , and when the electric field is \mathbf{E} .

On expanding the right hand side of Eq. (2) in a power series in the amplitude \mathring{E} , we obtain by the definition of (4)

$$I_n = I_{\sigma\tau} n_\sigma n_\tau, \quad (5)$$

where $I_{\sigma\tau}$ is the light scattering tensor of the form

$$I_{\sigma\tau} = \frac{1}{90R_0^2} \left(\frac{\omega}{c} \right)^4 \left\{ 5\mathring{E}_\sigma \mathring{E}_\tau F_{is} + (3\delta_{\sigma\tau} \mathring{E}^2 + \mathring{E}_\sigma \mathring{E}_\tau) F_{anis} + \right. \\ \left. + \frac{1}{84} [7\mathring{E}_\sigma \mathring{E}_\tau G_{is} + (3\delta_{\sigma\tau} \mathring{E}^2 + 5\mathring{E}_\sigma \mathring{E}_\tau) G_{anis}] \mathring{E}^2 + \dots \right\}. \quad (6)$$

Here, the factors (Kielich 1960)

$$F_{is} = \frac{1}{\omega^4} \left\langle \frac{\partial^2 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta} (\sigma_{\alpha\beta\gamma\delta} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle, \quad (7)$$

$$F_{anis} = \frac{1}{2\omega^4} \left\langle \frac{\partial^2 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta} (5\delta_{\alpha\beta} \delta_{\gamma\delta} - \sigma_{\alpha\beta\gamma\delta}) \right\rangle, \quad (8)$$

characterize the isotropic and anisotropic linear light scattering, respectively, and

$$G_{is} = \frac{1}{\omega^4} \left\langle \frac{\partial^4 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta \partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} (\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}) \right\rangle - \\ - \frac{2}{\omega^4 kT} \left\langle \frac{\partial^2 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta} \left\{ 3 \frac{\partial^2 \overline{U}}{\partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} (\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}) - \right. \right. \\ \left. \left. - \left\langle \frac{\partial^2 \overline{U}}{\partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} \right\rangle (7\sigma_{\alpha\beta\gamma\delta} - 20\delta_{\alpha\beta} \delta_{\gamma\delta}) \delta_{\epsilon\eta} \right\} \right\rangle, \quad (9)$$

$$G_{anis} = \frac{1}{2\omega^4} \left\langle \frac{\partial^4 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta \partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} (7\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta}) \right\rangle - \\ - \frac{1}{\omega^4 kT} \left\langle \frac{\partial^2 \overline{\dot{M}_\alpha \dot{M}_\beta}}{\partial \mathring{E}_\gamma \partial \mathring{E}_\delta} \left\{ 3 \frac{\partial^2 \overline{U}}{\partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} (7\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta}) - \right. \right. \\ \left. \left. - 7 \left\langle \frac{\partial^2 \overline{U}}{\partial \mathring{E}_\epsilon \partial \mathring{E}_\eta} \right\rangle (5\delta_{\alpha\beta} \delta_{\gamma\delta} - \sigma_{\alpha\beta\gamma\delta}) \delta_{\epsilon\eta} \right\} \right\rangle \quad (10)$$

— that of nonlinear light scattering.

In the above expressions we have introduced the following tensors:

$$\begin{aligned}\sigma_{\alpha\beta\gamma\delta} &= \delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}, \\ \sigma_{\alpha\beta\gamma\delta\epsilon\eta} &= \delta_{\alpha\beta}\sigma_{\gamma\delta\epsilon\eta} + \delta_{\alpha\gamma}\sigma_{\delta\epsilon\eta\beta} + \delta_{\alpha\delta}\sigma_{\epsilon\eta\beta\gamma} + \delta_{\alpha\epsilon}\sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta}\sigma_{\beta\gamma\delta\epsilon},\end{aligned}\quad (11)$$

with $\delta_{\alpha\beta}$ denoting the unit tensor and the brackets $\langle \rangle$ — the statistical average at zero electric field, as resulting from (4) for $E = 0$.

3. Depolarization ratio and Rayleigh's ratio

Let us now assume that the reference system XYZ is attached to the centre of the scattering volume V and the system $X'Y'Z'$ — to the point of observation of the scattered light. Consider a primary light beam travelling in the Y -axis direction with electric vector oscillating in the XZ -plane at an angle ψ to the plane of observation (XY -plane); thus, in the XYZ system

$$\mathbf{E} = (\mathbf{x} \cos \psi + \mathbf{z} \sin \psi) E, \quad (12)$$

where \mathbf{x} , \mathbf{y} and \mathbf{z} are unit vectors in the X , Y and Z directions, respectively. The light scattered is observed in the XY -plane at the angle ϑ with respect to the direction of incidence (Y -axis).

The intensity of the scattered components oscillating parallel and perpendicular to the plane of observation are defined as follows in the $X'Y'Z'$ system:

$$I_{\parallel} = I_{\sigma\tau}\mathbf{x}'\mathbf{x}'_{\tau}, \quad I_{\perp} = I_{\sigma\tau}\mathbf{z}'\mathbf{z}'_{\tau}.$$

Substituting herein the scattering tensor of Eq. (6) and using the fact that $\mathbf{x}' = \mathbf{x} \cos \vartheta - \mathbf{y} \sin \vartheta$ and $\mathbf{z}' = \mathbf{z}$, we obtain by Eq. (12)

$$\begin{aligned}I_{\parallel} &= \frac{1}{45R_0^2} \left(\frac{\omega}{c}\right)^4 \left\{ [5 \cos^2 \psi \cos^2 \vartheta F_{is} + (3 + \cos^2 \psi \cos^2 \vartheta) F_{anis}] I + \right. \\ &\quad \left. + \frac{1}{42} [7 \cos^2 \psi \cos^2 \vartheta G_{is} + (3 + 5 \cos^2 \psi \cos^2 \vartheta) G_{anis}^{\dagger}] I^2 + \dots \right\},\end{aligned}\quad (13)$$

$$\begin{aligned}I_{\perp} &= \frac{1}{45R_0^2} \left(\frac{\omega}{c}\right)^4 \left\{ [5 \sin^2 \psi F_{is} + (3 + \sin^2 \psi) F_{anis}] I + \right. \\ &\quad \left. + \frac{1}{42} [7 \sin^2 \psi G_{is} + (3 + 5 \sin^2 \psi) G_{anis}^{\dagger}] I^2 + \dots \right\},\end{aligned}\quad (14)$$

where $I = \frac{1}{2} \dot{\mathbf{E}}^2 = \dot{E}^2$ denotes the incident light intensity.

In Eqs (13) and (14) the first term proportional to I describe the linear light scattering and the second term with I^2 — the additional non-linear scattering produced by a strong light beam.

By Eqs (13) and (14), the depolarization ratio of the light scattered $D = I_{\parallel}/I_{\perp}$ is therefore given by

$$D = D_0 + D_1 I + \dots, \quad (15)$$

where

$$D_0 = \frac{5 \cos^2 \psi \cos^2 \vartheta F_{is} + (3 + \cos^2 \psi \cos^2 \vartheta) F_{anis}}{5 \sin^2 \psi F_{is} + (3 + \sin^2 \psi) F_{anis}} \quad (16)$$

is the depolarization ratio of linearly scattered light, and

$$D_1 = \frac{1}{42} \left\{ \frac{7 \cos^2 \psi \cos^2 \vartheta G_{is} + (3 + 5 \cos^2 \psi \cos^2 \vartheta) G_{anis}}{5 \sin^2 \psi F_{is} + (3 + \sin^2 \psi) F_{anis}} - D_0 \frac{7 \sin^2 \psi G_{is} + (3 + 5 \sin^2 \psi) G_{anis}}{5 \sin^2 \psi F_{is} + (3 + \sin^2 \psi) F_{anis}} \right\}. \quad (17)$$

determined the nonlinear influence on D due to the light beam of high intensity I .

If, in particular, the electric vector of the incident light beam oscillates in the plane of observation ($\psi = 0^\circ$), Eqs (16) and (17) become

$$D_0^{\parallel} = \frac{5 \cos^2 \vartheta F_{is} + (3 + \cos^2 \vartheta) F_{anis}}{3F_{anis}}, \quad (18)$$

$$D_1^{\parallel} = \frac{1}{126F_{anis}} \{(7G_{is} + 5G_{anis}) \cos^2 \vartheta + 3(1 - D_0) G_{anis}\}, \quad (19)$$

For incident light with plane of oscillation perpendicular to the plane of observation ($\psi = 90^\circ$), Eqs (16) and (17) reduce to

$$D_0^{\perp} = \frac{3F_{anis}}{5F_{is} + 4F_{anis}}, \quad (20)$$

$$D_1^{\perp} = \frac{(3 - 8D_0) G_{anis} - 7D_0 G_{is}}{42(5F_{is} + 4F_{anis})}. \quad (21)$$

In the case when the incident light is nonpolarized, $\cos^2 \psi$ and $\sin^2 \psi$ have to be replaced by $\frac{1}{2}$ in Eqs (16) and (17), yielding

$$D_0^n = \frac{5 \cos^2 \vartheta F_{is} + (6 + \cos^2 \vartheta) F_{anis}}{5F_{is} + 7F_{anis}}, \quad (22)$$

$$D_1^n = \frac{(6 + 5 \cos^2 \vartheta - 11D_0^n) G_{anis} + 7(\cos^2 \vartheta - D_0^n) G_{is}}{42(5F_{is} + 7F_{anis})}. \quad (23)$$

Analogously to Eq. (15), the Rayleigh ratio (or light scattering constant) can be expressed as follows:

$$S = \frac{(I_{\parallel} + I_{\perp}) R_0^2}{VI} \left(\frac{n^2 + 2}{3} \right)^2 = S_0 + S_1 I + \dots, \quad (24)$$

where, by Eqs (13) and (14), we have in general

$$S_0 = \frac{1}{45V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 \{5(1 - \cos^2 \psi \sin^2 \vartheta) F_{is} + (7 - \cos^2 \psi \sin^2 \vartheta) F_{anis}\}, \quad (25)$$

$$S_1 = \frac{1}{1890V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 \{7(1 - \cos^2 \psi \sin^2 \vartheta) G_{is} + (11 - 5 \cos^2 \psi \sin^2 \vartheta) G_{anis}\}, \quad (26)$$

with n denoting the refractive index of a spherical sample of volume V .

For incident light with oscillations in the plane of observation, we obtain from Eqs (25) and (26)

$$S_0^{\parallel} = \frac{1}{45V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 \{5 \cos^2 \vartheta F_{is} + (6 + \cos^2 \vartheta) F_{anis}\}, \quad (27)$$

$$S_1^{\parallel} = \frac{1}{1890V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 \{7 \cos^2 \vartheta G_{is} + (6 + 5 \cos^2 \vartheta) G_{anis}\}, \quad (28)$$

whereas for oscillations perpendicular to the plane of observation.

$$S_0^{\perp} = \frac{1}{45V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 (5F_{is} + 7F_{anis}), \quad (29)$$

$$S_1^{\perp} = \frac{1}{1890V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 (7G_{is} + 11G_{anis}). \quad (30)$$

When the primary beam is nonpolarized, Eqs (25) and (26) lead to the results

$$S_0^n = \frac{1}{90V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 \{5(1 + \cos^2 \vartheta) F_{is} + (13 + \cos^2 \vartheta) F_{anis}\}, \quad (31)$$

$$S_1^n = \frac{1}{3780V} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 \{7(1 + \cos^2 \vartheta) G_{is} + (17 + 5 \cos^2 \vartheta) G_{anis}\}. \quad (32)$$

4. Application to special cases and discussion

Using the fact that

$$\frac{d^2}{dt^2} (\cos \omega t)^n = -n\omega^2 \{n \cos^n \omega t - (n-1) \cos^{n-2} \omega t\},$$

we obtain by Eq. (1)

$$\begin{aligned} \ddot{m}_\alpha^{(p)} = & -\omega^2 \left(\alpha_{\alpha\beta}^{(p)} + \frac{1}{8} \gamma_{\alpha\beta\gamma\delta}^{(p)} \dot{E}_\gamma \dot{E}_\delta + \dots \right) \dot{E}_\beta \cos \omega t - \\ & - \frac{1}{4} (2\omega)^2 \beta_{\alpha\beta\gamma}^{(p)} \dot{E}_\beta \dot{E}_\gamma \cos 2\omega t - \frac{1}{24} (3\omega)^2 \gamma_{\alpha\beta\gamma\delta}^{(p)} \dot{E}_\beta \dot{E}_\gamma \dot{E}_\delta \cos 3\omega t - \dots \end{aligned} \quad (33)$$

We see that the electric dipole induced in the molecule by a strong optical field radiates in the first approximation with the fundamental frequency ω , whereas in further approximations — with the second harmonic frequency 2ω and third harmonic frequency 3ω .

By Eqs (3) and (33) and on time-averaging

$$\begin{aligned} \overline{(\cos \omega t)^2} &= \overline{(\cos 2\omega t)^2} = \overline{(\cos 3\omega t)^2} = \frac{1}{2}, \\ \overline{\cos \omega t \cos 2\omega t} &= \overline{\cos \omega t \cos 3\omega t} = 0, \end{aligned} \quad (34)$$

we have with the accuracy to \dot{E}^6

$$\begin{aligned} \overline{\dot{M}_\alpha \dot{M}_\beta} = & \frac{1}{2} \sum_{p=1}^N \sum_{q=1}^N \left\{ \omega^4 \left[\alpha_{\alpha\gamma}^{(p)} \alpha_{\beta\delta}^{(q)} + \frac{1}{8} (\alpha_{\alpha\gamma}^{(p)} \gamma_{\beta\delta\epsilon\eta}^{(q)} + \gamma_{\alpha\gamma\epsilon\eta}^{(p)} \alpha_{\beta\delta}^{(q)}) \dot{E}_\epsilon \dot{E}_\eta + \right. \right. \\ & \left. \left. + \frac{1}{64} \gamma_{\alpha\gamma\epsilon\eta}^{(p)} \gamma_{\beta\delta\theta\chi}^{(q)} \dot{E}_\epsilon \dot{E}_\eta \dot{E}_\theta \dot{E}_\chi + \dots \right] + \frac{1}{16} (2\omega)^4 \beta_{\alpha\gamma\epsilon}^{(p)} \beta_{\beta\delta\eta}^{(q)} \dot{E}_\epsilon \dot{E}_\eta + \right. \\ & \left. + \frac{1}{576} (3\omega)^4 \gamma'_{\alpha\gamma\epsilon\eta}^{(p)} \gamma'_{\beta\delta\theta\chi}^{(q)} \dot{E}_\epsilon \dot{E}_\eta \dot{E}_\theta \dot{E}_\chi + \dots \right\} \dot{E}_\epsilon \dot{E}_\delta. \end{aligned} \quad (35)$$

The terms with ω^4 describe the Rayleigh light scattering (linear and nonlinear in the light intensity $I = \frac{1}{2} \dot{E}^2$), while the terms containing $(2\omega)^4$ and $(3\omega)^4$ correspond to the nonlinear second-harmonic and third-harmonic scattered radiation, respectively.

In the same approximation as that used in (1), the time-averaged potential energy of system is:

$$\overline{U(\tau, \mathbf{E})} = U(\tau, 0) - \frac{1}{4} \sum_{p=1}^N \alpha_{\alpha\beta}^{(p)} \dot{E}_\alpha \dot{E}_\beta - \dots, \quad (36)$$

where $U(\tau, 0)$ is the total potential energy of the system in the absence of an electric field.

Substitution of Eq. (35) and Eq. (36) into Eqs (7)—(10) leads to

$$F_{is} = \left\langle \sum_{p=1}^N \sum_{q=1}^N \alpha_{\alpha\alpha}^{(p)} \alpha_{\beta\beta}^{(q)} \right\rangle, \quad (37)$$

$$F_{anis} = \frac{1}{2} \left\langle \sum_{p=1}^N \sum_{q=1}^N (3\alpha_{\alpha\beta}^{(p)} \alpha_{\alpha\beta}^{(q)} - \alpha_{\alpha\alpha}^{(p)} \alpha_{\beta\beta}^{(q)}) \right\rangle, \quad (38)$$

$$\begin{aligned} G_{is} = & \frac{1}{2} \left\langle 3 \sum_{p=1}^N \sum_{q=1}^N \{3(\alpha_{\alpha\alpha}^{(p)} \gamma_{\beta\beta\gamma\gamma}^{(q)} + \gamma_{\alpha\alpha\beta\beta}^{(p)} \alpha_{\gamma\gamma}^{(q)}) + 8(5\beta_{\alpha\beta\gamma}^{(p)} \beta_{\alpha\beta\gamma}^{(q)} - 2\beta_{\alpha\alpha\beta\beta}^{(p)} \beta_{\beta\gamma\gamma}^{(q)})\} + \right. \\ & \left. + \frac{4}{kT} \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N \{ \alpha_{\alpha\alpha}^{(p)} (3\alpha_{\beta\gamma}^{(q)} \alpha_{\beta\gamma}^{(r)} - \alpha_{\beta\beta}^{(q)} \alpha_{\gamma\gamma}^{(r)}) + \alpha_{\alpha\alpha}^{(q)} (3\alpha_{\beta\gamma}^{(p)} \alpha_{\beta\gamma}^{(r)} - \alpha_{\beta\beta}^{(p)} \alpha_{\gamma\gamma}^{(r)}) \} \right\rangle, \end{aligned} \quad (39)$$

$$\begin{aligned} G_{anis} = & \frac{1}{4} \left\langle 3 \sum_{p=1}^N \sum_{q=1}^N \{3(3\alpha_{\alpha\beta}^{(p)} \gamma_{\alpha\beta\gamma\gamma}^{(q)} - \alpha_{\alpha\alpha}^{(p)} \gamma_{\beta\beta\gamma\gamma}^{(q)} + 3\gamma_{\alpha\beta\gamma\gamma}^{(p)} \alpha_{\alpha\beta}^{(q)} - \gamma_{\alpha\alpha\beta\beta}^{(p)} \alpha_{\gamma\gamma}^{(q)}) + \right. \\ & \left. + 16(4\beta_{\alpha\beta\gamma}^{(p)} \beta_{\alpha\beta\gamma}^{(q)} - \beta_{\alpha\alpha\beta\beta}^{(p)} \beta_{\beta\gamma\gamma}^{(q)})\} + \frac{4}{kT} \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N \{9\alpha_{\alpha\beta}^{(p)} \alpha_{\alpha\gamma}^{(q)} \alpha_{\beta\gamma}^{(r)} - \right. \\ & \left. - 3(\alpha_{\alpha\alpha}^{(p)} \alpha_{\beta\gamma}^{(q)} \alpha_{\beta\gamma}^{(r)} + \alpha_{\alpha\beta}^{(p)} \alpha_{\gamma\gamma}^{(q)} \alpha_{\alpha\beta}^{(r)} + \alpha_{\alpha\beta}^{(p)} \alpha_{\alpha\beta}^{(q)} \alpha_{\gamma\gamma}^{(r)}) + 2\alpha_{\alpha\alpha}^{(p)} \alpha_{\beta\beta}^{(q)} \alpha_{\gamma\gamma}^{(r)}\} \right\rangle. \end{aligned} \quad (40)$$

Further simplification of the foregoing factors can be achieved by assuming a particular type of symmetry in the scattering molecules (see, Appendix B). This will be now effected for the cases most commonly occurring.

4.1 Optically isotropic molecules or atoms

In the case of isotropically polarizable molecules the molecular factors of anisotropic light scattering (38) and (40) vanish and those of isotropic light scattering (37) and (39) assume the following simpler form

$$F_{\text{is}} = 9 \left\langle \sum_{p=1}^N \sum_{q=1}^N \alpha^{(p)} \alpha^{(q)} \right\rangle = 9\alpha^2 N(1 + G_R), \quad (41)$$

$$G_{\text{is}} = \frac{135}{2} \left\langle \sum_{p=1}^N \sum_{q=1}^N (\alpha^{(p)} \gamma^{(q)} + \gamma^{(p)} \alpha^{(q)}) \right\rangle = 135\alpha\gamma N(1 + G_R), \quad (42)$$

where $\alpha = \frac{1}{3} \alpha_{\alpha\alpha}$ and $\gamma = \frac{1}{5} \gamma_{\alpha\alpha\beta\beta}$ are the mean polarizability and hyperpolarizability, respectively.

In the above formulas the Zernike-Prins (1927) parameter has been introduced

$$G_R = 4\pi\rho \int_0^\infty \{g(r_{pq}) - 1\} r_{pq}^2 dr_{pq} = \rho kT\beta_T - 1, \quad (43)$$

describing the radial correlation of the molecules; $\rho = N/V$ is the molecule number density, $g(r_{pq})$ — the radial correlation function for molecules p and q separated by a distance r_{pq} , and β_T — the isothermal compressibility coefficient of the medium.

Substitution of (41) and (42) into Eqs (31) and (32) yields

$$S_0^n = \frac{1}{2} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 \alpha^2 \rho (1 + G_R) (1 + \cos^2 \vartheta) = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} kT\beta_T (1 + \cos^2 \vartheta), \quad (44)$$

$$S_1^n = \frac{1}{2} \left(\frac{\gamma}{\alpha} \right) S_0^n. \quad (45)$$

Eq. (44) is the Einstein-Smoluchowski-Rocard formula which for $G_R = 0$ reduces to the well-known result of Rayleigh (*cf.* Cabannes 1929).

By (44) and (45), the Rayleigh ratio can be rewritten in the form

$$\frac{S^n - S_0^n}{S_0^n} = \frac{1}{2} \left(\frac{\gamma}{\alpha} \right) I. \quad (46)$$

Thus, investigation of the relative change in S produced by a strong light beam of intensity I makes possible to determine directly the value of the hyperpolarizability γ of an isotropic molecule.

We shall now evaluate the change in S for methane. Using the data (Buckingham and Pople 1955) $\alpha = 2.4 \times 10^{-24}$ cm³ and $\gamma = 2.6 \times 10^{-36}$ e. s. u., we have by (46) $(S^n - S_0^n)/S_0^n = 0.5 \times 10^{-12} I$ and we see that the change of S is very small being of the order of 10^{-8} for a light beam of the high intensity of $I = 2 \times 10^4$ e. s. u.

4.2 Molecules of tetrahedral symmetry

For molecules possessing the tetrahedral symmetry (*e. g.* CH₄), $F_{\text{anis}} = 0$ and F_{is} is again given by (41), whereas G_{is} and G_{anis} are of the form (if radial correlation only exists in the system)

$$G_{\text{is}} = 9N\{15\alpha\gamma(1+G_R) - 16\beta_{123}^2\}, \quad (47)$$

$$G_{\text{anis}} = 288N\beta_{123}^2, \quad (48)$$

and we have by Eqs (22) and (23)

$$D_0^n = \cos^2 \vartheta, \quad D_1^n = \frac{32}{35} \left(\frac{1 - \cos^2 \vartheta}{1 + G_R} \right) \left(\frac{\beta_{123}}{\alpha} \right)^2. \quad (49)$$

If the scattered light is observed perpendicularly to the direction of incidence ($\vartheta = 90^\circ$), the above expressions yield for $G_R = 0$

$$D^n = \frac{32}{35} \left(\frac{\beta_{123}}{\alpha} \right)^2 I. \quad (50)$$

In the case of carbon tetrachloride we have (Kielich 1962) $\alpha = 10.5 \times 10^{-24} \text{ cm}^3$, $\rho = 6.23 \times 10^{21} \text{ cm}^{-3}$ and $\beta_T = 105 \times 10^{-12} \text{ cgs}$. Thus, calculating the parameter G_R from Eq. (43) and assuming $\beta_{123} = 3 \times 10^{-30} \text{ e. s. u.}$, we obtain on the basis of (49), for $\vartheta = 90^\circ$ $D^n = 3 \times 10^{-12} I$.

4.3 Axially symmetric molecules with a centre of inversion

Assuming that the molecules are axially symmetric and possess a centre of inversion we obtain from Eqs (37)–(40) in the absence of angular correlation of the molecules of the scattering system

$$F_{\text{is}} = 9\alpha^2 N(1+G_R), \quad F_{\text{anis}} = 9\alpha^2 \kappa_\alpha^2 N. \quad (51)$$

$$G_{\text{is}} = 27\alpha N \left(5\gamma + \frac{8}{kT} \alpha^2 \kappa_\alpha^2 \right) (1+G_R), \quad (52)$$

$$G_{\text{anis}} = \frac{27}{2} \alpha \kappa_\alpha N \left(7\gamma \kappa_\gamma + \frac{4}{kT} \alpha^2 \kappa_\alpha^2 \right), \quad (53)$$

where $\kappa_\alpha = (\alpha_{33} - \alpha_{11})/3\alpha$ is the anisotropy of polarizability of the axially symmetric molecule and $\kappa_\gamma = 2(3\gamma_{3333} + 3\gamma_{1133} - 4\gamma_{1111})/21\gamma$ — its anisotropy of hyperpolarizability.

Using the above expressions and assuming for simplicity that the incident beam is polarized with oscillations in the plane of observation and that the scattered light is observed at an angle of $\vartheta = 90^\circ$, we obtain by Eqs (27) and (28)

$$\frac{S_{\parallel} - S_0^{\parallel}}{S_0^{\parallel}} = \frac{1}{2} \left\{ \frac{\gamma \kappa_\gamma}{\alpha \kappa_\alpha} + \frac{4\alpha \kappa_\alpha}{7kT} \right\} I, \quad (54)$$

where

$$S_0^{\parallel} = \frac{6}{5} \left(\frac{\omega}{c} \right)^4 \left(\frac{n^2+2}{3} \right)^2 \alpha^2 \kappa_a^2 \rho = \frac{6\pi^2(n^2-1)^2}{5\lambda^4 \rho} \kappa_a^2. \quad (55)$$

The first term in Eq. (54) describes the contribution to S resulting from the effect of optical hyperpolarizability and the second term — that from the effect of molecular optical orientation.

We see that Eq. (55) provides a simple method of measuring the value of the polarizability anisotropy κ_a , whereas Eq. (54) yields the value of the hyperpolarizability anisotropy κ_γ of the molecule.

We now proceed to determine the order of magnitude of the change S for carbon disulphide, for which we have the following data (Buckingham and Raab 1957): $\alpha = 8.6 \times 10^{-24} \text{ cm}^3$, $\kappa_a = 0.25$ and $\gamma = 54.4 \times 10^{-36}$ e. s. u. Assuming $\kappa_\gamma = \kappa_a$ (the anisotropy of hyperpolarizability of the CS_2 molecule is not known), we obtain from (54) for $T = 300^\circ \text{K}$: $(S^{\parallel} - S_0^{\parallel})/S_0^{\parallel} = (3.1 + 13.7) \times 10^{-12} I = 3 \times 10^{-7}$ for $I = 2 \times 10^4$ e. s. u.

4.4 Axially symmetric molecules without centre of inversion

If the axially symmetric molecules have no centre of inversion, we obtain in addition to Eqs. (52) and (53), on neglecting the molecular correlations,

$$G_{\text{is}} = 12\beta^2 N \left(\frac{2}{3} + 16\kappa_\beta - 20\kappa_\beta^2 \right), \quad (56)$$

$$G_{\text{anis}} = 12\beta^2 N (19 - 32\kappa_\beta + 40\kappa_\beta^2), \quad (57)$$

where $\beta = (\beta_{333} + 2\beta_{113})/3$ and $\kappa_\beta = (\beta_{333} - \beta_{113})/3\beta$ are the mean hyperpolarizability and the anisotropy of hyperpolarizability of the molecule, respectively.

From (22) and (23), for $\vartheta = 90^\circ$, we find by Eqs (51)—(53) with $G_R = 0$ and (56)—(57)

$$\frac{D^n - D_0^n}{D_0^n} = -\frac{1}{24} \left\{ \left(\frac{\gamma}{\alpha\kappa_a} \right) [10\kappa_a^{-1} D_0 + (11D_0 - 6)\kappa_\gamma] + \frac{8}{63} \left(\frac{\beta}{\alpha\kappa_a} \right)^2 \left[7 \left(\frac{2}{3} + 16\kappa_\beta - 20\kappa_\beta^2 \right) D_0 + (11D_0 - 6)(19 - 32\kappa_\beta + 40\kappa_\beta^2) \right] + \frac{4\alpha}{7kT} [28D_0 + (11D_0 - 6)\kappa_a] \right\} I, \quad (58)$$

where $D_0 = 6\kappa_a^2/(5+7\kappa_a^2)$ is the usual depolarization ratio of a gas (Cabannes 1929).

For chloroform we have (Bhagavantam 1942) $D_0 = 1.8 \times 10^{-2}$, (Landolt-Börnstein 1951) $\alpha = 8.23 \times 10^{-24} \text{ cm}^3$, $\kappa_a = -0.094$ and (Kielich 1962) $\beta = 11.3 \times 10^{-29}$ e.s.u., $\kappa_\beta = -0.074$ (the values of γ and κ_γ are not known for the CHCl_3 molecule), so that Eq. (58) yields $(D^n - D_0^n)/D_0^n = (134 - 0.1) \times 10^{-10} I$. It will be seen that in the case of CHCl_3 the important contribution to D^n arises from the first hyperpolarizability β , whereas the contribution from the orientational molecular effect is very small and so plays practically no part at all here. From the above evaluation for CHCl_3 the change in D is of 10^{-4} for $I = 10^4$ e.s.u. and ought to be conveniently accessible to measurement, since as estimated by Andrews.

and Buckingham (1960) changes of 10^{-6} in the depolarization ratio of gaseous systems should be detectable with a photomultiplier tube.

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APPENDIX A

Frequency-dependence of the hyperpolarizability tensors

Suppose the molecule to be subjected to perturbations by an oscillating electric field $\mathbf{E} = \hat{\mathbf{E}} \cos \omega t$, so that its total Hamiltonian is

$$H = H_0 - \frac{1}{2} (\boldsymbol{\mu} \cdot \mathbf{E}^+ + \boldsymbol{\mu} \cdot \mathbf{E}^-), \quad (\text{A.1})$$

with H_0 denoting the Hamiltonian of the nonperturbed molecule having the electric dipole moment operator $\boldsymbol{\mu}$ and $\mathbf{E}^+ = \hat{\mathbf{E}} e^{i\omega t}$ and $\mathbf{E}^- = \hat{\mathbf{E}} e^{-i\omega t}$.

The α -component of the oscillating dipole moment of the molecule in a ground state g can be expanded, to within the third-order time-dependent perturbation calculus, as follows:

$$m_\alpha = \sum_{nk} \{ (\delta_{ng} a_k^{(1)} + a_n^{(1)*} \delta_{kg}) + (\delta_{ng} a_k^{(2)} + a_n^{(1)*} a_k^{(1)} + a_n^{(2)*} \delta_{kg}) + (\delta_{ng} a_k^{(3)} + a_n^{(1)*} a_k^{(2)} + a_n^{(2)*} a_k^{(1)} + a_n^{(3)*} \delta_{kg}) + \dots \} \mu_{\alpha nk} e^{i\omega_{nk} t}, \quad (\text{A.2})$$

where the coefficients $a_n^{(1)}$, $a_n^{(2)}$, ... are functions of the time and can be calculated to the order $s+1$ by integrating the following differential equation:

$$i\hbar \dot{a}_n^{(s+1)} = - \frac{1}{2} \sum_k (\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^+ + \boldsymbol{\mu}_{nk} \cdot \mathbf{E}^-) a_k^{(s)} e^{i\omega_{nk} t}, \quad (\text{A.3})$$

Here $\boldsymbol{\mu}_{nk} = \int \psi_n^* \boldsymbol{\mu} \psi_k d\tau$ is the matrix element of the electric dipole moment associated with the transition $n \rightarrow k$ between the quantum states n and k whose nonperturbed wave functions are ψ_n and ψ_k , respectively; $\omega_{nk} = \omega_n - \omega_k$ is the Bohr frequency corresponding to the transition $n \rightarrow k$.

With the foregoing expressions m_α may be written in the form of expansion (1), with the polarizability tensor

$$\alpha_{\alpha\beta} \hat{E}_\beta \cos \omega t = \frac{1}{2\hbar} \sum_n \left\{ \frac{\mu_{\alpha gn} (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \pm \omega)} - \frac{\mu_{\alpha ng} (\boldsymbol{\mu}_{gn} \cdot \mathbf{E}^\mp)}{(\omega_{gn} \mp \omega)} \right\} \quad (\text{A.4})$$

and the following hyperpolarizability tensors:

$$\beta'_{\alpha\beta\gamma} \hat{E}_\beta \hat{E}_\gamma = \frac{1}{\hbar^2} \sum_{nk} \left\{ \frac{\mu_{\alpha gk} (\boldsymbol{\mu}_{kn} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp)}{\omega_{kg} (\omega_{ng} \mp \omega)} + \frac{\mu_{\alpha nk} (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \mp \omega) (\omega_{kg} \mp \omega)} + \frac{\mu_{\alpha ng} (\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\pm)}{\omega_{ng} (\omega_{kg} \mp \omega)} \right\},$$

$$\begin{aligned}
\beta_{\alpha\beta\gamma} \dot{E}_\beta \dot{E}_\gamma \cos 2\omega t &= \frac{1}{\hbar^2} \sum_{nk} \left\{ \frac{\mu_{\alpha g k} (\boldsymbol{\mu}_{kn} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm)}{(\omega_{kg} \pm 2\omega) (\omega_{ng} \pm \omega)} + \right. \\
&\quad \left. + \frac{\mu_{\alpha nk} (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \mp \omega) (\omega_{kg} \pm \omega)} + \frac{\mu_{\alpha ng} (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \pm 2\omega) (\omega_{kg} \pm \omega)} \right\}, \\
\gamma_{\alpha\beta\gamma\delta} \dot{E}_\beta \dot{E}_\gamma \dot{E}_\delta \cos \omega t &= \frac{1}{\hbar^3} \sum_{nkl} \left\{ \mu_{\alpha g k} \left[\frac{(\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ln} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp)}{(\omega_{kg} \pm \omega) \omega_{lg} (\omega_{ng} \mp \omega)} + \right. \right. \\
&\quad \left. \left. + \frac{(\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ln} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm)}{(\omega_{kg} \pm \omega) \omega_{lg} (\omega_{ng} \pm \omega)} + \frac{(\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ln} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp)}{(\omega_{kg} \mp \omega) (\omega_{lg} \mp 2\omega) (\omega_{ng} \mp \omega)} \right] + \right. \\
&\quad + \mu_{\alpha nk} \left[\frac{(\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \pm \omega) (\omega_{kg} \pm 2\omega) (\omega_{lg} \pm \omega)} + \frac{(\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \pm \omega) \omega_{kg} (\omega_{lg} \mp \omega)} + \right. \\
&\quad \left. + \frac{(\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \mp \omega) \omega_{kg} (\omega_{lg} \mp \omega)} + \frac{(\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{nl} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{kg} \pm \omega) (\omega_{ng} \pm 2\omega) (\omega_{lg} \pm \omega)} + \right. \\
&\quad \left. + \frac{(\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{kg} \pm \omega) \omega_{ng} (\omega_{lg} \mp \omega)} + \frac{(\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{nl} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{kg} \mp \omega) \omega_{ng} (\omega_{lg} \mp \omega)} \right] + \\
&\quad + \mu_{\alpha ng} \left[\frac{(\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \pm \omega) \omega_{kg} (\omega_{lg} \mp \omega)} + \frac{(\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \pm \omega) \omega_{kg} (\omega_{lg} \pm \omega)} + \right. \\
&\quad \left. \left. + \frac{(\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \mp \omega) (\omega_{kg} \mp 2\omega) (\omega_{lg} \mp \omega)} \right] \right\}, \\
\gamma'_{\alpha\beta\gamma\delta} \dot{E}_\beta \dot{E}_\gamma \dot{E}_\delta \cos 3\omega t &= \frac{3}{\hbar^3} \sum_{nkl} \left\{ \frac{\mu_{\alpha g k} (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ln} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm)}{(\omega_{kg} \pm 3\omega) (\omega_{lg} \pm 2\omega) (\omega_{ng} \pm \omega)} + \right. \\
&\quad + \mu_{\alpha nk} \left[\frac{(\boldsymbol{\mu}_{ng} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\pm) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\pm)}{(\omega_{ng} \mp \omega) (\omega_{kg} \pm 2\omega) (\omega_{lg} \pm \omega)} + \frac{(\boldsymbol{\mu}_{kg} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{nl} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{kg} \mp \omega) (\omega_{ng} \pm 2\omega) (\omega_{lg} \pm \omega)} \right] + \\
&\quad \left. + \frac{\mu_{\alpha ng} (\boldsymbol{\mu}_{nk} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{kl} \cdot \mathbf{E}^\mp) (\boldsymbol{\mu}_{lg} \cdot \mathbf{E}^\mp)}{(\omega_{ng} \pm 3\omega) (\omega_{kg} \pm 2\omega) (\omega_{lg} \pm \omega)} \right\}, \tag{A. 5}
\end{aligned}$$

where, for brevity, the notation

$$\frac{\mathbf{E}^\pm}{\omega_{ng} \pm \omega} = \frac{\mathbf{E}^+}{\omega_{ng} + \omega} + \frac{\mathbf{E}^-}{\omega_{ng} - \omega}, \text{ etc.} \tag{A. 6}$$

is used.

For the general case of two or three light waves at different frequencies the permutation symmetry relations and the frequency dependence of the tensors $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are developed and discussed by Armstrong *et al.* (1962).

APPENDIX B

Polarizability and hyperpolarizability tensors for spherical, tetrahedral and axially symmetric molecules

For molecules possessing the spherical symmetry, the tensors $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ assume the form (Buckingham and Stephen 1957).

$$\alpha_{\alpha\beta} = \alpha\delta_{\alpha\beta}, \quad \beta_{\alpha\beta\gamma} = 0, \quad \gamma_{\alpha\beta\gamma\delta} = \frac{1}{3}\gamma\sigma_{\alpha\beta\gamma\delta}, \quad (\text{B.1})$$

where the tensor $\sigma_{\alpha\beta\gamma\delta}$ is defined by (11).

In the case of molecules possessing the tetrahedral symmetry we have

$$\begin{aligned} \alpha_{\alpha\beta} &= \alpha\delta_{\alpha\beta}, \\ \beta_{\alpha\beta\gamma} &= \beta_{123}\{i_\alpha(j_\beta k_\gamma + k_\beta j_\gamma) + j_\alpha(k_\beta i_\gamma + i_\beta k_\gamma) + k_\alpha(i_\beta j_\gamma + j_\beta i_\gamma)\}, \\ \gamma_{\alpha\beta\gamma\delta} &= \gamma_{1133}\sigma_{\alpha\beta\gamma\delta} + (\gamma_{1111} - 3\gamma_{1133})(i_\alpha i_\beta i_\gamma i_\delta + j_\alpha j_\beta j_\gamma j_\delta + k_\alpha k_\beta k_\gamma k_\delta), \end{aligned} \quad (\text{B.2})$$

with \mathbf{i} , \mathbf{j} and \mathbf{k} denoting unit vectors along the axes 1, 2 and 3 of the molecular reference system.

For the case of molecules symmetric with respect to the molecular z -axis, the tensor components of $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ can be expressed as follows:

$$\begin{aligned} \alpha_{\alpha\beta} &= \alpha(1 - \kappa_\alpha)\delta_{\alpha\beta} + 3\alpha\kappa_\alpha k_\alpha k_\beta, \\ \beta_{\alpha\beta\gamma} &= \beta(1 - \kappa_\beta)(\delta_{\alpha\beta} k_\gamma + \delta_{\beta\gamma} k_\alpha + \delta_{\gamma\alpha} k_\beta - 2k_\alpha k_\beta k_\gamma) + 3\beta\kappa_\beta k_\alpha k_\beta k_\gamma, \\ \gamma_{\alpha\beta\gamma\delta} &= \frac{1}{3}\gamma(1 - \kappa_\gamma)\sigma_{\alpha\beta\gamma\delta} + \frac{1}{2}\gamma\kappa_\gamma(\delta_{\alpha\beta} k_\gamma k_\delta + \delta_{\alpha\gamma} k_\beta k_\delta + \\ &\quad + \delta_{\alpha\delta} k_\beta k_\gamma + \delta_{\beta\gamma} k_\alpha k_\delta + \delta_{\beta\delta} k_\alpha k_\gamma + \delta_{\gamma\delta} k_\alpha k_\beta) + \\ &\quad + \frac{1}{35}(\gamma_{3333} - 6\gamma_{1133} + \gamma_{1111})\{35k_\alpha k_\beta k_\gamma k_\delta - 5(\delta_{\alpha\beta} k_\gamma k_\delta + \delta_{\alpha\gamma} k_\beta k_\delta + \\ &\quad + \delta_{\alpha\delta} k_\beta k_\gamma + \delta_{\beta\gamma} k_\alpha k_\delta + \delta_{\beta\delta} k_\alpha k_\gamma + \delta_{\gamma\delta} k_\alpha k_\beta) + \sigma_{\alpha\beta\gamma\delta}\}. \end{aligned} \quad (\text{B.3})$$

On applying the above expressions we obtain for axially symmetric molecules

$$\begin{aligned} 3\alpha_{\alpha\beta}^{(p)}\alpha_{\alpha\beta}^{(q)} - \alpha_{\alpha\alpha}^{(p)}\alpha_{\beta\beta}^{(q)} &= 9\alpha^2\kappa_\alpha^2\{3(\mathbf{k}_p \cdot \mathbf{k}_q)^2 - 1\}, \\ 3\alpha_{\alpha\beta}^{(p)}\gamma_{\alpha\beta\gamma\gamma}^{(q)} - \alpha_{\alpha\alpha}^{(p)}\gamma_{\beta\beta\gamma\gamma}^{(q)} &= \frac{7}{2}\alpha\kappa_\alpha\gamma\kappa_\gamma\{3(\mathbf{k}_p \cdot \mathbf{k}_q)^2 - 1\}, \\ 3\alpha_{\alpha\beta}^{(p)}\alpha_{\alpha\gamma}^{(q)}\alpha_{\beta\gamma}^{(r)} - 3(\alpha_{\alpha\alpha}^{(p)}\alpha_{\beta\beta}^{(q)}\alpha_{\beta\gamma}^{(r)} + \alpha_{\alpha\beta}^{(p)}\alpha_{\gamma\gamma}^{(q)}\alpha_{\alpha\beta}^{(r)} + \alpha_{\alpha\beta}^{(p)}\alpha_{\alpha\beta}^{(q)}\alpha_{\gamma\gamma}^{(r)}) + \\ + 2\alpha_{\alpha\alpha}^{(p)}\alpha_{\beta\beta}^{(q)}\alpha_{\gamma\gamma}^{(r)} &= 27\alpha^3\kappa_\alpha^3\{9(\mathbf{k}_p \cdot \mathbf{k}_q)(\mathbf{k}_q \cdot \mathbf{k}_r)(\mathbf{k}_r \cdot \mathbf{k}_p) - \\ &\quad - 3[(\mathbf{k}_p \cdot \mathbf{k}_q)^2 + (\mathbf{k}_q \cdot \mathbf{k}_r)^2 + (\mathbf{k}_r \cdot \mathbf{k}_p)^2] + 2\}, \\ \beta_{\alpha\beta\gamma}^{(p)}\beta_{\alpha\beta\gamma}^{(q)} &= 9\beta^2(\mathbf{k}_p \cdot \mathbf{k}_q)^3 - \beta^2(1 - \kappa_\beta)(1 + 5\kappa_\beta)\{5(\mathbf{k}_p \cdot \mathbf{k}_q)^2 - 3\}(\mathbf{k}_p \cdot \mathbf{k}_q), \\ \beta_{\alpha\alpha\beta}^{(p)}\beta_{\beta\gamma\gamma}^{(q)} &= 9\beta^2(\mathbf{k}_p \cdot \mathbf{k}_q), \end{aligned} \quad (\text{B.4})$$

where \mathbf{k}_p is the unit vector along the axis of symmetry of molecule p .

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